

## Conference Paper

# 1D NiO-SnO<sub>2</sub> Heterojunction Nanofibers as Acetone Sensor

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## Abstract

1D NiO-SnO<sub>2</sub> nanofibers with p-n heterostructure were synthesized by electrospinning with post-synthetic heat treatment. The morphology and composition were characterized by scanning electron microscope, X-ray diffraction, and energy dispersive X-ray spectrometry. A possible growth model was proposed to describe the formation of hierarchical NiO-SnO<sub>2</sub>. The gas sensors based on NiO-SnO<sub>2</sub> exhibited p-type response to acetone. The excellent acetone sensing properties may be attributed to numerous p-n junctions between NiO and SnO<sub>2</sub> nanograins as well as the unique architecture. The changes of energy level and space charge layer of NiO-SnO<sub>2</sub> heterojunction nanofibers when exposed to acetone are described in detail.

**Keywords:** NiO-SnO<sub>2</sub>; Electrospinning; Heterojunctions; Acetone

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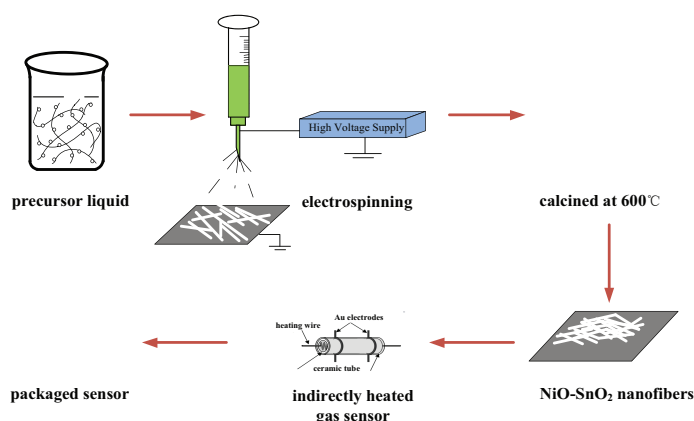
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## 1. Introduction

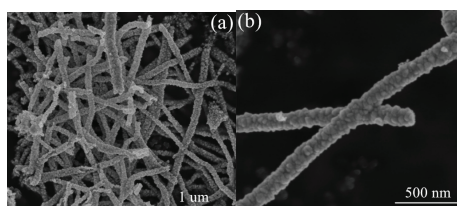
In recent years, nanomaterials with heterojunction structures which is conducive to the enhancement of sensing performance of a single component, have attracted wide attention in the field of gas sensors due to the synergistic effects induced by the coupling and the heterointerface between two different classes of nanomaterials [1]. As heterostructured nanomaterials have strong heterointeraction between the closely packed interface nanounits, their properties cannot be considered as a simple contact of the individual components, but more complex and more superior [2]. As a p-type semiconductor with an energy gap of 4.2 eV, there have been a large number of researches focusing on the gas sensing characteristics of different NiO-SnO<sub>2</sub> nanostructures, and results have exhibited enhanced sensitivities compared to the single component [3-5]. However, the discussion about the interface bonds at the p-n heterointerface that can facilitate electron transfer is not detailed.

In this report, an acetone gas sensor based on hierarchical NiO-SnO<sub>2</sub> nanofibers was fabricated by electrospinning. XRD results showed that NiO-SnO<sub>2</sub> was formed without any other impurity peaks. Hierarchical nanofibers composed of tiny nanocrystals were clearly observed from the SEM images. Meanwhile, the sensing response of the NiO-SnO<sub>2</sub> heterostructure manifested as NiO do, namely p-type response. In addition, electrochemical impedance spectroscopy was also examined to demonstrate the differentiation in the interface resistance of the NiO-SnO<sub>2</sub> nanofibers.

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**Figure 1:** Schematic of the fabrication process of NiO-SnO<sub>2</sub> composite nanofibers based gas sensors.



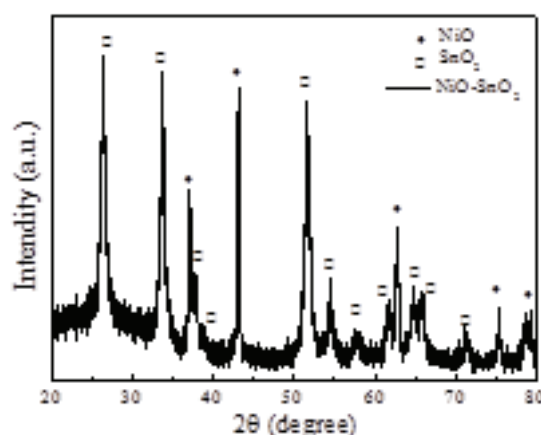
**Figure 2:** SEM images of NiO-SnO<sub>2</sub> nanofibers (a) with low magnification and (b) with high magnification.

## 2. Experimental Details

In a typical procedure for preparing NiO-SnO<sub>2</sub> composite nanofibers, precursor solution with a molar rate of 1:1, 0.36 g SnCl<sub>2</sub>·2H<sub>2</sub>O and 0.464 g Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O were dissolved in 4.7 mL of EtOH solvent at room temperature with magnetic stirring for 30 minutes. Subsequently, 0.824 g PVP and 3.9 mL of DMF were added into above solution, agitating for 24 h until a viscous emerald green precursor solution completely formed. The electrospinning parameters were as follows: the voltage and the distance between the needle (positive pole) and the collector (negative pole) were 20 kV and 15 cm, respectively. The ambient temperature and relative humidity were 14.5°C and 33 %RH. The diameter of the needle was 0.7 mm. In order to decompose PVP completely, the as-synthesized nanofibers were sintered at 600°C for 3 h in air with a slow heating rate of 1°C/min. Fig. 1 illustrates the complete schematic of NiO-SnO<sub>2</sub> composite nanofibers based gas sensors by simple electrospinning.

## 3. Characterization Results

Fig. 2 (a) and (b) display the SEM images of NiO-SnO<sub>2</sub> nanofibers with low magnification and high magnification, respectively. It can be seen that after calcination, the surface of the nanofibers becomes rough and is self-assembled by numerous graded nanoparticles.



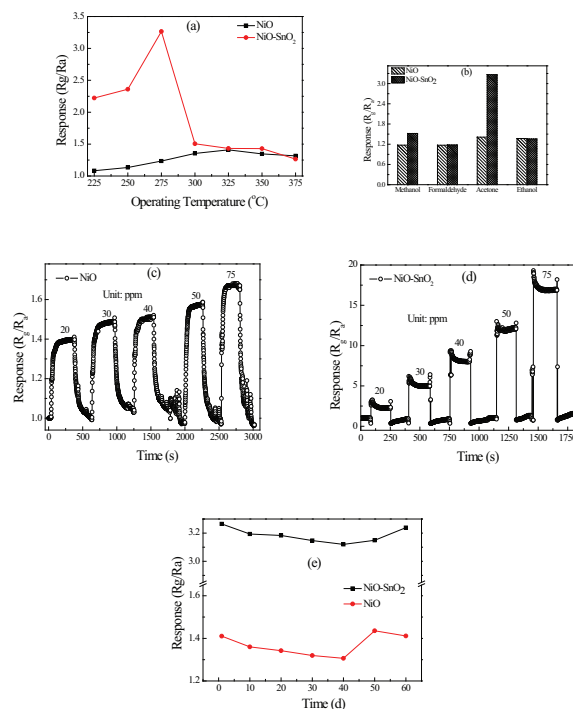
**Figure 3:** XRD patterns of NiO-SnO<sub>2</sub> nanofibers.

XRD patterns of NiO-SnO<sub>2</sub> nanofibers are shown in Fig. 3. It can be seen that the NiO-SnO<sub>2</sub> composite nanofibers have two crystalline phases of tetragonal SnO<sub>2</sub> (JCPDF#99-0024) and cubic NiO (JCPDF#73-1523) simultaneously, indicating that the calcination temperature of 600°C is sufficient to remove PVP completely and form the two oxides.

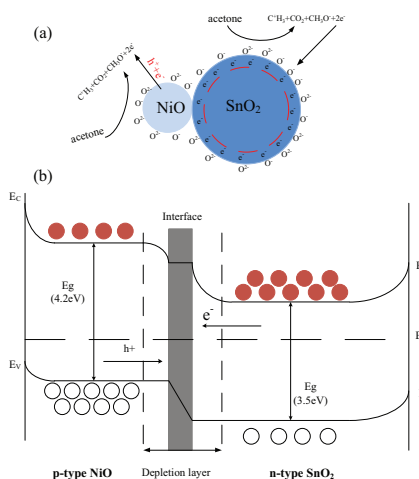
#### 4. Gas Sensing Properties and Mechanism

Fig. 4 (a) shows that the gas sensor based on NiO-SnO<sub>2</sub> nanofibers has a maximum gas response at the operating temperature of 275°C, while the sensor based on NiO shows highest responses at 325°C. As a result, 275°C and 325°C were respectively selected as the operating temperature for NiO-SnO<sub>2</sub> and NiO sensors in the following gas testing process. From Fig. 4 (b) it can be clearly seen that NiO-SnO<sub>2</sub> exhibits a better selectivity than NiO, having a preferential response to acetone. It implies that NiO-SnO<sub>2</sub> could be used as a very promising candidate for selective acetone detection. The transient acetone sensing characteristics of NiO and NiO-SnO<sub>2</sub> in a range of 20-75 ppm at their own optimal operating temperatures are shown in Fig. 4 (c) and (d), respectively. Furthermore, the long-time stability of NiO and NiO-SnO<sub>2</sub> are also measured. Both sensors exhibit good stability towards 20 ppm acetone in 60 days, as shown in Fig. 4 (e).

The enhanced acetone sensing properties of NiO-SnO<sub>2</sub> nanofibers may be ascribed to the formation of p-n junction between p-type NiO and n-type SnO<sub>2</sub> nanograins. The energy band structure of the NiO-SnO<sub>2</sub> heterojunction is shown schematically in Fig. 5 (b), without taking into account the interface states. In order to obtain equalization of Fermi levels, a relative motion of carriers, namely electronics flowing from SnO<sub>2</sub> to NiO, while holes in the opposite direction occur in the physical interface between p-type NiO and n-type SnO<sub>2</sub>, resulting in band bending. At the same time, an electronic depletion layer has been formed on the surface of SnO<sub>2</sub> while an electronic accumulation layer on the side of NiO, as shown in Fig. 5 (b). Before introducing acetone, the oxygen molecules in air will capture electrons from the conduction bands of both



**Figure 4:** (a) Responses of the sensors based on NiO and NiO-SnO<sub>2</sub> nanofibers to 10 ppm acetone as a function of operating temperature. (b) Responses of NiO and NiO-SnO<sub>2</sub> to various gases including methanol, formaldehyde, acetone and ethanol. (c)(d) Dynamic sensing response of NiO and NiO-SnO<sub>2</sub> to acetone in a range of 20-75 ppm. (e) Stability of NiO and NiO-SnO<sub>2</sub> to 20 ppm acetone.



**Figure 5:** (a) Schematic model for the p-type NiO/n-type SnO<sub>2</sub> heterostructure based sensor when exposed to acetone. (b) Proposed band structure for p-type NiO/n-type SnO<sub>2</sub> heterostructure.  $E_c$ : lower level of conduction band;  $E_f$ : Fermi level;  $E_v$ : upper level of valance band.

SnO<sub>2</sub> and NiO. The adsorption of oxygen results in the further widening of electron depletion layer and hole depletion layer on the surface of SnO<sub>2</sub> and NiO, respectively. Therefore, compared with bare NiO, the NiO-SnO<sub>2</sub> nanofibers perform with a much higher initial resistance due to the p-n heterojunction effect. Upon exposure to acetone gas, the acetone molecules react with chemically adsorbed oxygen ions and release

the captured electrons back to Ni vacancies; thereby the resistance of the NiO-SnO<sub>2</sub> nanofibers increases. Herein, according to the significantly increased initial resistance and the degenerated in the equivalent hole concentration of the NiO-SnO<sub>2</sub> nanofibers due to the p-n heterojunction effect, the sensitivity of the NiO-SnO<sub>2</sub> nanofibers toward acetone will obviously improve.

## 5. Conclusion

In order to obtain as more p-n heterojunction as possible, heterojunction nanofibers with 1:1 molar ratio of NiO to SnO<sub>2</sub> were fabricated via simple electrospinning technique. It was found that the NiO-SnO<sub>2</sub> nanofibers exhibited an enhanced p-type response to acetone compared to bare NiO. The p-type sensitivity of NiO-SnO<sub>2</sub> nanofibers may be ascribed to the more NiO content than SnO<sub>2</sub>. Basing on the heterojunction theory, the initial resistance of NiO-SnO<sub>2</sub> nanofibers is higher than that of bare NiO due to the equalization of different Fermi levels. Meanwhile, the built-in electrical field at the heterojunction can effectively block the acetone adsorption-induced local electrons in the SnO<sub>2</sub> to NiO, which contributes to the increasing of equivalent hole concentration in the NiO-SnO<sub>2</sub> nanofibers and then leads to the improvement of sensitivities.

## Acknowledgement

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